PYROLYSIS GC/MS ANALYSIS OF LOW-RANK COAL

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ABSTRACT

The reactivity of coals under liquefaction conditions is related to their thermal decomposition. Pyrolysis GC/MS is used to determine the identity of the volatile products as the changes in coal structure occur. A Wyoming subbituminous coal (Clovis Point) and a North Dakota lignite (Indian Head) were heated under helium at four temperatures (160 °C, 250 °C, 300 °C, and 350 °C) for 30 minutes. The volatile species were cryogenically trapped in a capillary gas chromatographic column for GC/MS analysis. The two lower temperatures showed only devolatilization products (e.g., biological markers such as alkanes and terpenoids) while the higher temperatures yielded products resulting from bond-breaking (i.e., pyrolysis). The devolatilization and pyrolysis products of the two coals were similar in overall composition but markedly different in their distribution. The subbituminous coal (Clovis Point) pyrolysate contained phenol and cresols along with large amounts of C_{19} to C_{31} normal alkanes. Indian Head lignite pyrolysate contained a much larger amount of phenol, alkyl substituted phenols and dihydroxybenzene and lesser amounts of C_{19} to C_{31} alkanes.

INTRODUCTION

Pyrolysis gas chromatography/mass spectrometry has become increasingly popular for the analysis of solid fuel and fuel related materials. In recent papers, pyrolysis-GC/MS has been applied to model compounds (1), asphaltenes (2), kerogens (2), buried wood (3), coalified logs (3), and coal(4). A wide variety of techniques are employed for the pyrolysis of the sample. Most of the reported techniques employ some type of pyrolysis probe capable of rapid heating rates and temperatures in the 600 °C to >1000 °C range. The sample sizes reported were from 5 ug to 100 ug.

In order to study the products of thermal decomposition under low-severity liquefaction conditions, the maximum temperature used in this study was 350 °C. Our technique involves the use of approximately 10 mg of sample per analysis. The devolatilization and pyrolysis products are introduced into a split injector and cryogenically trapped at the head of a fused silica capillary gas chromatographic column. The use of a relatively large sample, 10 mg, and a split injector allows for a more representative sample to be collected on the capillary column. The sample is then separated and analyzed using standard GC/MS techniques.

EXPERIMENTAL

Samples

Wyoming subbituminous coal (Clovis Point) and a North Dakota lignite (Indian Head) were used in this study. Both coals were ground to -200 mesh and dried in a vacuum desiccator for 48 hours prior to pyrolysis.

Pyrolysis Gas Chromatography/Mass Spectrometry

Figure 1 shows a schematic diagram of the pyrolysis apparatus. Approximately 10 mg of coal was placed in a 30 cm x 4 mm i.d. pyrex tube. The sample was positioned approximately 5 cm from the outlet of the pyrex tube with a plug of silanized glass wool. The outlet of the tube was attached to a 1/4" x 1/16" stainless steel union fitted with a 2 in. x 0.20 mm i.d. needle. The sample tube was placed in the tube heater that had been preheated to the desired pyrolysis temperature. During the pyrolysis step, the needle was inserted into the split/splitless injection port, the helium flow was diverted from the injection port to sweep the pyrolysis products out of the pyrolysis chamber and into the injection port, and the tube heater was dropped down around the sample and union/needle assembly. The injection port was operated with a split ratio of approximately 1:100. The pyrolysate entering the fused-silica capillary chromatographic column was cryogenically trapped by holding the oven temperature at -50 ^{o}C during the 30 minutes pyrolysis. Upon completion of pyrolysis, the column oven was heated rapidly to 0 ^{o}C followed by temperature programming at 6 ^{o}C/min to 320 ^{o}C. GC/MS analysis of the pyrolysis products was performed with a Hewlett-Packard model 5985B using a 60 m x 0.25 mm i.d. (0.25 um film thickness) DB-5 fused silica capillary column (J & W Scientific, Folsom, CA). Helium was used as the carrier gas at an approximate linear flow rate of 50 cm/sec. Pyrolysis gas chromatography with flame ionization detection (GC/FID) was performed in a similar manner using a Hewlett-Packard 5890 GC.

Electron impact (EI) mass spectra were generated at 70 eV with a scan range of 35-500 amu. In the chemical ionization (CI) mode, reagent gas was introduced directly into the source through a heated transfer line colinear with the chromatographic column. Source pressure and CI tuning parameters have been reported previously (7). The structures of the dioxygen compounds (e.g., C_2 dihydroxybenzene vs C_1 methoxyphenol) were confirmed by the use of deuterated reagent chemical ionization GC/MS. In this technique, the -OH proton is exchanged for deuterium and an apparent molecular weight change occurs. For example, a C_2 dihydroxybenzene (MW = 138) would exhibit a pseudo-molecular ion at m/z 142 (ionization by D^+ and exchange of two acidic protons for deuterium), while a C_1 methoxyphenol (MW = 138) would have a pseudo-molecular ion at m/z 141 (ionization by D^+ and exchange of one acidic proton). Because of a prominent background ion at m/z

101 due to a reagent cluster ($(CH_3OD)_3D^+$), the lower limit for the mass scan range using CH_3OD CI was 104 amu.

RESULTS AND DISCUSSION

Figures 2 and 3 are the pyrolysis-GC/FID chromatograms of the Wyoming subbituminous coal and the North Dakota lignite at the four pyrolysis temperatures (160, 250, 300, and 350 °C). The numbered peaks in Figures 2 and 3 are identified in Table 1. Chromatograms for 160 °C and 250 °C show species that are thermally desorbed from the coal, and that are not pyrolysis products. This has been confirmed by the use of supercritical N_2O extraction (300 atm at 45 °C) (8) which yielded extracts that had chromatograms virtually identical to those from the 160 °C and 250 °C thermal experiments. These compounds are primarily biological markers such as alkanes, sesquiterpenes, triterpanes and steranes(5,6).

Comparison of the chromatograms obtained at 350 °C for the two coals shows marked differences in the composition of their pyrolysates. The pyrolysate yield for the lignite under the pyrolysis conditions described in the experimental section was much less then the yield for the subbituminous coal. The pyrolysate from the Wyoming subbituminous coal contains relatively larger amounts of aliphatics, aromatics, and oxygen-containing species such as phenol and alkylphenols. Catechol (1,2-dihydroxybenzene) is present in the pyrolysate of both coals, but in much lower concentration from the subbituminous coal than from the lignite. The lignite pyrolysate contains the same types of compounds as those found in the subbituminous coal pyrolysate but the distribution is very different. Alkanes in the range of C_{18} to C_{31} are present in both pyrolysates but are in much lower concentration in the lignite pyrolysis product. Anisole and C_1 anisole isomers were present in the lignite pyrolysate but not in the subbituminous pyrolysate. Larger amounts (relative to other components in the sample) of dihydroxybenzene, methoxyphenol, and their C_1 and C_2 alkyl derivatives were present in the lignite pyrolysate. This is consistent with results published by Hatcher, et al (3), and would be expected since lower rank coals have undergone less coalification and would contain organic constituents which more closely resemble structures (e.g., lignin) found in the original plant material. Several of the substituted dihydroxybenzenes and methoxyphenols were absent from the subbituminous pyrolysate.

CONCLUSION

Pyrolysis gas chromatography/mass spectrometry can be a valuable tool for evaluating candidate coals for use in synthetic fuel processes especially where separation and upgrading of the pyrolysate fraction is a concern and the chemistry of the process has a narrow operational range. Structural differences in the pyrolysates can be related to the structure of the coals. The larger sample size and split injection used in our technique

allows for a more representative sample to be analyzed.

CREDIT

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TABLE I. Identification of Numbered Peaks from Figures 2 and 3.

Peak Number	Species
1	methylcyclopentadiene or isomer
2	benzene
3	acetic acid
4	C_2-cyclopentadiene or isomer
5	toluene
6	C_2-cyclohexane or isomer
7	C_2-benzene
8	cyclooctatetraene and C_2-benzene
9	anisole
10	phenol
11	C_1-anisole
12	C_3-benzene
13,14	cresol isomers
15	methoxyphenol
16	C_2-phenol
17	dihydroxybenzene
18	C_3-benzene
19	C_1-dihydroxybenzene and C_1-methoxyphenol
20	C_1-dihydroxybenzene
21,22	C_2-dihydroxybenzene
23	C_2-naphthalene
24	cadalene
25	M=266 biological marker
26-39	C_{18} to C_{31} alkanes
40,41,42	M=206 sesquiterpene isomers
43	M=262 biological marker
44	M=276 biological marker
45	M=270 biological marker
46	M=252 biological marker
47	M=234 biological marker
48	M=286 biological marker

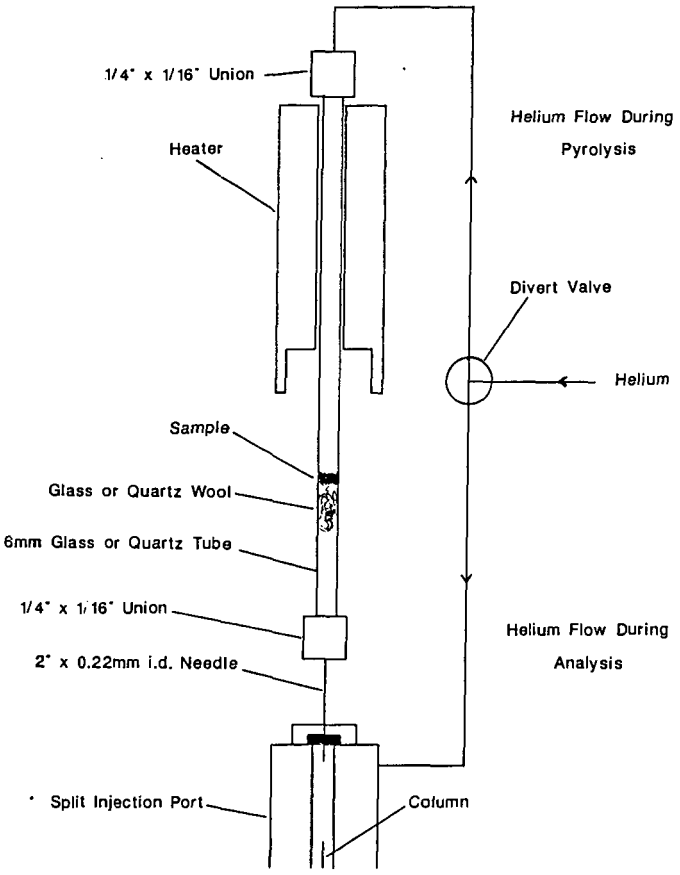

Figure 1. Pyrolysis Apparatus.

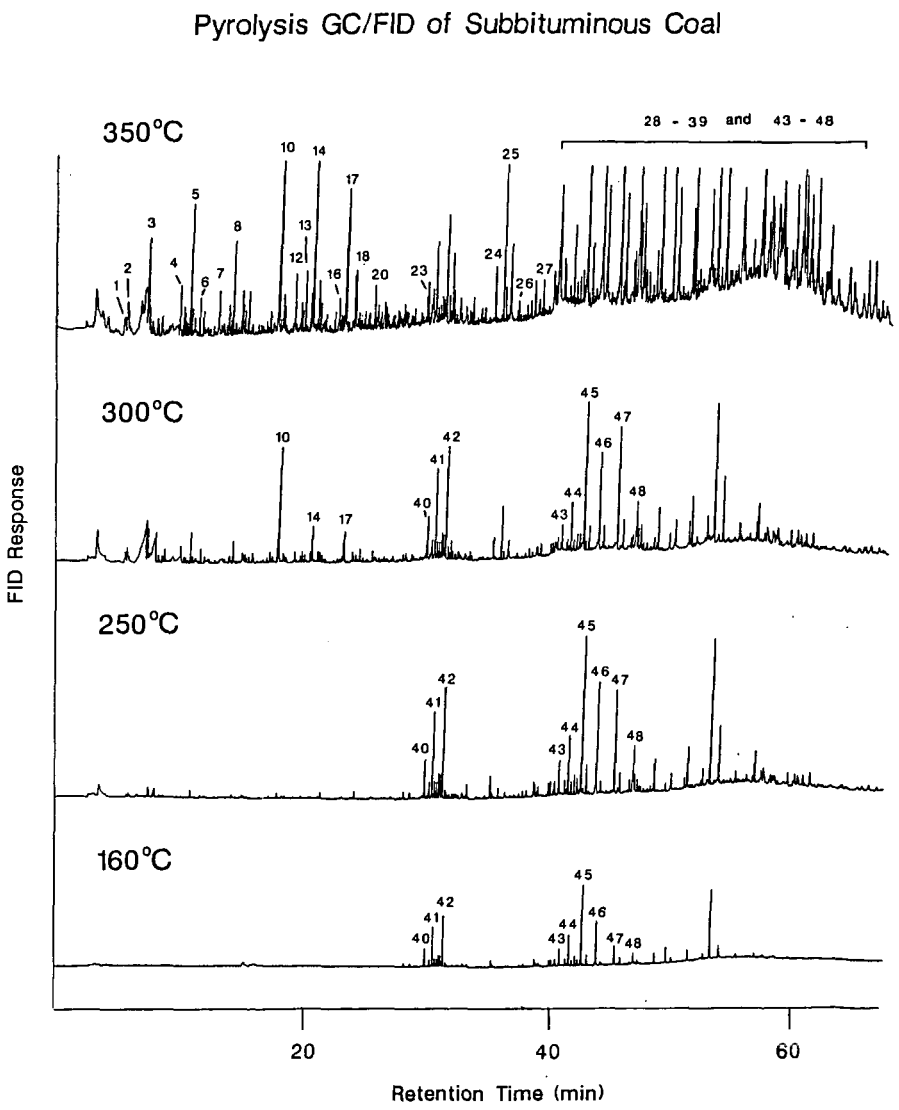

Figure 2. Pyrolysis GC/FID trace from Wyoming subbituminous coal.

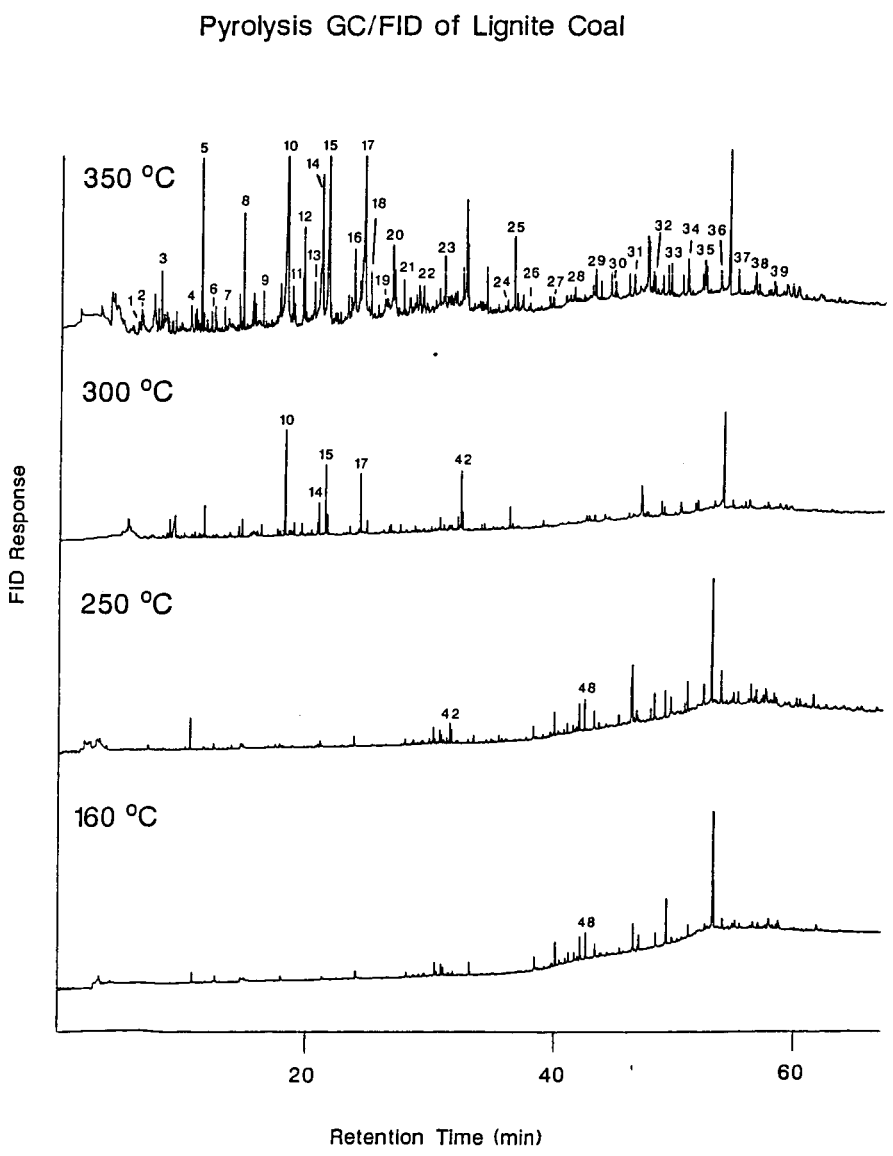

Figure 3. Pyrolysis GC/FID trace from North Dakota lignite.